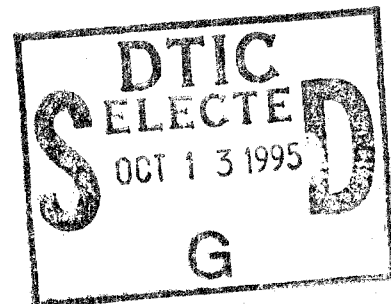


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METALLURGY DIVISION

August 1959



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NRL MEMORANDUM REPORT 964

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BY

M. C. BLOOM, B. F. BROWN
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ABSTRACT

Boiler tubes from the USS EDWARDS (DD-950) have been examined in the laboratory in order to account for a failure after 600-750 hours of steaming. The results of metallographic, x-ray diffraction, and chemical analyses are reported. The probable cause of the rapid attack is suggested.

PROBLEM STATUS

This report completes one phase of the problem. Work on other aspects is continuing.

AUTHORIZATION

NRL PROBLEM NUMBER M01-08

BUREAU PROBLEM NUMBER S-F013-0616

INTRODUCTION

Four failed tubes from boiler 1B of the U.S.S. EDWARDS (DD-950) were examined by chemical and microscopic methods. Each of these tubes had areas which had bulged under pressure, and it was requested that the probable cause of the failures be ascertained, and that possible future remedies be suggested.

Since no such tube failure had occurred in boiler 1A, which was reported to have been run under identical conditions, it was requested that sections of tubing be removed for examination and comparison with tubes from boiler 1B. Outwardly, the tubes from boiler 1A appeared intact, but internal corrosion was severe. These tubes, also, were examined carefully.

NOTES ON METALLURGICAL EXAMINATIONS OF GENERATING TUBES

The generating tube failures were characteristically highly localized bulges terminating in ruptures. The ruptures can be identified as resulting from a relatively slow process (creep) and not from a momentary stoppage of circulation. Part of the evidence for this is the multiple grain-boundary voiding of Figure 1. Both Fig. 1 and Fig. 2 clearly demonstrate that the tube at that point was well in excess of 1335°F. One bulge which had not ruptured was sectioned (Fig. 3) and indicated that it too had been heated above 1335°, but probably not as high as the area of Fig. 1. The areas of overheating and bulging coincided exactly. A short distance away from a bulge there was no evidence of partial austenitization (Fig. 4). The tube wall was considerably reduced in thickness along the cylindrical element containing the bulges by a water-side reaction, and a thick white deposit coated that area. The deposit was especially thick at the bulges (Fig. 5). In boiler 1B this thick white layer was covered by a dark deposit of normal boiler-corrosion products.

There was no evidence of methanation such as had been seen in desuperheaters suffering comparable corrosion rates.

The fire-side of the tubes appeared to have been at least partially cleaned before being shipped to the Laboratory, which would eliminate any possibility of deriving evidence of fireside effects.

DESCRIPTION OF DEPOSITS

Tubes from boiler 1B had on their inner surfaces two identifiable layers of deposit. The dark outer layer appeared to be soft and fluffy, while the inner layer was hard, white, and crystalline, and was concentrated in the regions of failures.

Since the fluffy deposit seemed to be quite thick, measurements were made at a number of points. It was found that the deposit was by no means uniform in thickness, as are deposits which have been laid down gradually over a long period of time, but were actually very spotty, being somewhat more dense in the regions closest to the mud drum and almost disappearing (about 4 microns thick) at the ends of the tubes away from the mud drum. The maximum deposit thickness occurred at a point about 15" from the mud-drum ends of tubes examined. At this point the deposits were about 80 microns thick.

Tubes from boiler 1A had been drastically corroded. Such deposits as were present did not mask the large, interconnected, sharp-edged pits which covered the fire-side wall of the inner surfaces of the tubes. A gray-white powder lightly covered the entire surface, but was heaviest on the fire-side wall. The dark, fluffy deposit found in tubes from boiler 1B was entirely absent.

IDENTIFICATION OF DEPOSITS

A. Identification by X-Ray Diffraction: The white deposits from the two boilers gave x-ray diffraction patterns which were identical in all major details. This fact would imply that similar conditions had existed at the time the crystals had formed from materials present in the boilers.

Although none of the x-ray data could be fitted into those listed in the X-Ray Card Index, it was possible to synthesize several compounds which accounted for most of the lines appearing in the diffraction pattern. From comparisons, it was concluded that the white material consisted of two major crystalline phases: sodium pyrophosphate, and the reaction product of sodium pyrophosphate (or disodium-hydrogen phosphate) with metallic iron. Some of the chemistry of these materials is given below.

Using dilute nitric acid as a solvent, it was possible to extract the white, crystalline material, leaving behind a dark, magnetic powder. X-ray wise, this black material was found to be an iron-rich spinel mixed with metallic copper.

B. Chemical Analysis of Deposits: The white deposit was separated by physical methods into a magnetic and non-magnetic fraction for the purpose of intensifying x-ray patterns, and some of this material was submitted for chemical analysis. The results of these analyses are given in Table 1. The concentrations of sodium and phosphate are sufficiently high to permit detection of well-crystallized material by x-ray diffraction methods. The high iron content of the non-magnetic fraction would indicate that there is also present

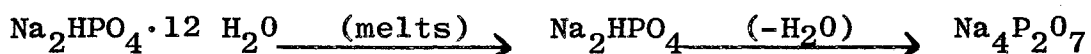
an unidentified colorless compound of iron. In all probability, this compound is a double salt with sodium, since no sign of iron oxides, phosphates, or pyrophosphates appeared in the crystal study of the white deposits.

The dark fluffy deposit from boiler 1B gave a spectroscopic analysis not differing markedly in constituents from the deposits found in normal boilers.

THE CHEMISTRY OF THE WHITE DEPOSITS

Sodium pyrophosphate was prepared for x-ray diffraction studies by the dehydration of disodium hydrogen phosphate at a moderate temperature. On being heated, the disodium-phosphate hydrate first melts, then boils, with the evolution of water, and finally becomes a dry powder which does not sinter or melt at a red heat. The product is sodium pyrophosphate.

The reaction proceeds as follows:



When trisodium phosphate is treated in the same manner there is a loss of water of crystallization, but no further reaction. In other words, the sodium pyrophosphate of the boiler deposit could not have formed under conditions of high pH (high sodium), but rather, under conditions of low pH (high phosphate).

In order to find what effect, if any, the disodium-hydrogen phosphate could have on iron at elevated temperatures, some powdered iron and disodium-hydrogen phosphate were heated together. As the temperature was brought up to the boiling point of the melted hydrate, a violent reaction set in, with a strong evolution of gas. The iron reacted completely, giving an off-white reaction product which showed no residual magnetism. X-ray diffraction analysis of this reaction product gave a pattern very nearly matching that of the white deposits of the boilers. The exact nature of the compounds formed is not known at this time.

It should be pointed out that phosphate/caustic ratios of the order sufficient to produce the kind of attack described above could be produced not only by the dehydration of concentrated boiler water containing Na_2HPO_4 without caustic addition, but also by similar dehydration of solutions containing other phosphates which require more caustic for neutralization, if these had been used as treatment chemicals with insufficient caustic additions. Such phosphates as sodium tripolyphosphate, sodium metaphosphate, sodium-dihydrogen phosphate, sodium hexametaphosphate, or sodium trimetaphosphate all fall in this category.

A similar reaction was attempted using trisodium phosphate and powdered iron, but even after sintering at a red heat, metallic iron remained, and there was no sign of a change in the x-ray diffraction pattern of the products of reaction.

When some disodium-hydrogen phosphate was heated on the surface of a section of tube from boiler 1B, the oxide in contact with the melt was removed completely, and the metal beneath was attacked.

CONCLUSIONS

The following conclusions are based on microscopic, chemical, and x-ray diffraction data described above:

1. The two boilers in question have not had the same history, since the white deposits in boiler 1B are covered with a darker, poorly crystallized material, while white deposits of boiler 1A are exposed.
2. It is probable that at the time the white material was laid down, the two boilers were operating under about the same conditions, and that these were conditions of very high phosphate and relatively low pH.
3. It is probable that the corrosion in boiler 1A was a direct result of the accumulation of soluble boiler-treatment chemicals in the generating tubes while the temperatures were high. This could be the result of steam blanketing and film boiling. The loss of a great deal of metal with little build-up of corrosion products would imply that the attack was chemical in nature, while the fact that the attack was localized on the fire-side wall of the tubes would imply that the concentration of chemicals occurred at this point.
4. It is probable that some of the damage in boiler 1B was due to chemical attack, but that the actual burnout of the tubes was due to suspensions from the mud drum being flushed out into the generator tubes, and adhering to the heated surfaces. The fact that the deposits were not uniform, but were very spotty, points to this probability, as does the fact that there is a decrease in total deposit as a function of distance from the mud drum. The ultimate cause of the failures could have been insufficient blowdown following the introduction of large excesses of water-treatment chemicals.

High localized heat fluxes (as, for example, from channeling of flue gases or from spalling of fireside deposit) could also have initiated localized hot spots. As these bulged, the steam blanket which formed within them permitted the wall temperature to rise well above the design temperature, leading to a stress-rupture failure.

5. The unusual chemical attack of the type noted here is apparently the result of high phosphate/caustic ratios in the water treatment.

COMMENTS

With proper attention to boiler-water chemistry such failures as these should not occur. Retubing the entire boiler is probably unnecessary; perhaps consideration should be given to a judicious sampling of unfailed generating tubes to ascertain the extent of phosphate attack. A thorough cleaning to remove the existing deposit should be followed by an inspection of the waterside to ensure that the deposit has been removed. The high localizations in heat flux believed to be directly responsible for the failures probably did not prevail in many tubes. Perhaps less efficient cleaning on the fireside in the failure areas would help prevent more failures if spalling of external deposits is the main cause of random burnouts in the generating tubes.

The obvious remedies for deleterious water-side deposits are:

1. Strict adherence to specified water chemistry.
2. Frequent and copious blowdowns to remove solids from the mud drum.

TABLE 1. SPECTROGRAPHIC SEMI-QUANTITATIVE ANALYSIS OF DEPOSIT
(Total Phosphate by Wet-Chemical Methods)

	White Deposit from Boiler 1A	Non-magnetic Portion of White Deposit of Boiler 1A
Fe	>10%	>10%
Na	<10	>10
Ca	<10	<10
Al	<1	<10
Cu	<10	<10
Mg	<1	<1
Si	<1	<1
Zn	<1	<1
Cr	<1	<1
V	<1	<0.1
Mn	<1	<1
Ni	<1	<1
Mo	<1	<1
Ag	<0.01	<1
Ti, Co, Pb	<0.1	<0.1
Total $\text{PO}_4^{=}$	14.1	16.6

TABLE II. TABULATION OF X-RAY DIFFRACTION DATA OF DEPOSITS,
AND OF PRINCIPAL LINES OF SOME PHOSPHATES

White Deposit Boiler 1A		White Deposit Boiler 1B		Synthetic Na ₄ P ₂ O ₇		Reaction Product of Fe and Na ₄ P ₂ O ₇		Na ₃ PO ₄		Na ₄ P ₂ O ₇ ·10 H ₂ O	
d(A)	I/I ₀	d(A)	I/I ₀	d(A)	I/I ₀	d(A)	I/I ₀	d(A)	I/I ₀	d(A)	I/I ₀
4.47	10	4.47	15	-	-	-	-	-	-	-	-
4.39	10	4.39	10	4.38	100	4.38	100	-	-	4.395	100
4.23	2	-	-	4.24	55	4.24	55	4.20	100	-	-
3.695	25	3.695	25	3.695	20	3.365	30	-	-	3.695	30
2.826	2	-	-	-	-	-	-	-	-	3.076	30
2.729	70	2.729	60	2.731	50	2.726	60	-	-	2.826	40
2.704	75	2.704	50	2.695	60	2.690	65	2.680	45	2.630	75
2.575	100	2.575	100	2.333	40	2.608	65	2.535	90	2.530	15
2.517	15	2.517	20	-	-	2.326	15	-	-	2.439	10
2.10	5	2.10	5	-	-	-	-	-	-	-	-
1.876	10	1.876	15	1.916	75	1.914	20	-	-	-	-
1.847	15	1.847	10	-	-	-	-	-	-	-	-

EXAMINATION OF DESUPERHEATER TUBES

Sections of desuperheater tubes from the 1A, 1B, and 2B boilers were submitted to the U. S. Naval Research Laboratory for investigation of a pitting attack on the watersides. The tubes from the 1A boiler were coated with bright-red corrosion products while those from the 1B and 2B boilers were coated with yellow corrosion products. X-ray diffraction patterns of the surfaces of tube specimens from each boiler revealed the complete absence of high temperature corrosion products on the watersides of specimens from the 1B and 2B boilers. It is concluded, therefore, that the tubes from these two boilers had been cleaned, and thus any possible clues to the cause of pitting have been removed.

The x-ray diffraction pattern on the tube specimen from the 1A boiler indicated the presence of hematite and magnetite. A white deposit present in some of the pits could not be identified. Metallographic examination showed the pits to be non-selective with regard to grain boundaries, and often devoid of corrosion products. Such an attack is characteristic of excessive corrosion which results in spalling of the scale and the setting up of localized concentration cells. The excessive corrosion is attributed to faulty water chemistry.

NOTES ON SUGGESTED REQUIREMENTS FOR SPECIMENS

Since every investigation of boiler failures and the accompanying corrosion problems requires a great deal of deductive reasoning based on the evidence found upon examination of the samples submitted, together with operating history, there is an urgent need for as complete a knowledge of the history of the specimens as can be obtained.

It is therefore recommended that the procedures given below be followed, whenever possible, in securing specimens for examination, in order to insure that the maximum amount of information be obtainable from the laboratory analysis.

(1) Provide a pencil sketch or other reliable description of the general location of the failure with respect to other parts of the boiler, and measure and record the distances of cuts from tube sheets when tubes are cut out. Labelling and numbering should be either self explanatory or clearly related to the sketch or recorded description.

(2) Do not disturb deposits either internal or external any more than necessary, even when the deposits do not seem to be obviously related to the cause of failure.

(3) Remove tubes by sawing rather than burning if at all possible, since considerable quantities of molten metal oxides and external deposits may be blown down a tube during burning and can later confuse the deductions made by laboratory examination.

(4) Plug both ends of tubes prior to shipment for examination, and whenever possible, wrap the tube in paper to preserve external deposits.

(5) Note and record details of handling a specimen during or after shutdown of a boiler, particularly when such details are unusual. (For example, if the fireside of a boiler was hosed down with sea water after shutdown, later examination of failed tubes might show considerable amounts of salt, although this chemical may have had no relation to the failure.)

(6) Provide as detailed a record as possible of operational and boiler-chemistry history along with general notes on the specific specimen.

FIGURE CAPTIONS

- Fig. 1 - 1B Boiler - RW No. 21 (Section through bulge that cracked). Note grain-boundary voids which are a result of prolonged exposure to high temperatures and stress. Etchant: 1% Nital. 500X.
- Fig. 2 - 1B Boiler - RW No. 21 (Section through bulge that had cracked). Notice structure indicating that metal was rapidly cooled from temperature above 1335°F when the tube failed. Etchant: 1% Nital. 1000X.
- Fig. 3 - 1B Boiler - RW No. 18 (Section through bulge that had not cracked). Note lamellar (new) pearlite which indicates that service temperature exceeded 1335°F. Etchant: 1% Nital plus 2% Picral. 1000X.
- Fig. 4 - 1B Boiler - RW No. 18 (Section adjacent to bulge). Note coarse carbides; no evidence of partial austenitization is present. Etchant: 1% Nital plus 2% Picral. 1000X.
- Fig. 5 - 1B Boiler - RW No. 30, Waterside (Section containing two bulges). Note configuration of deposits around bulges and massive deposits over the actual bulges. (2-1/4 X).

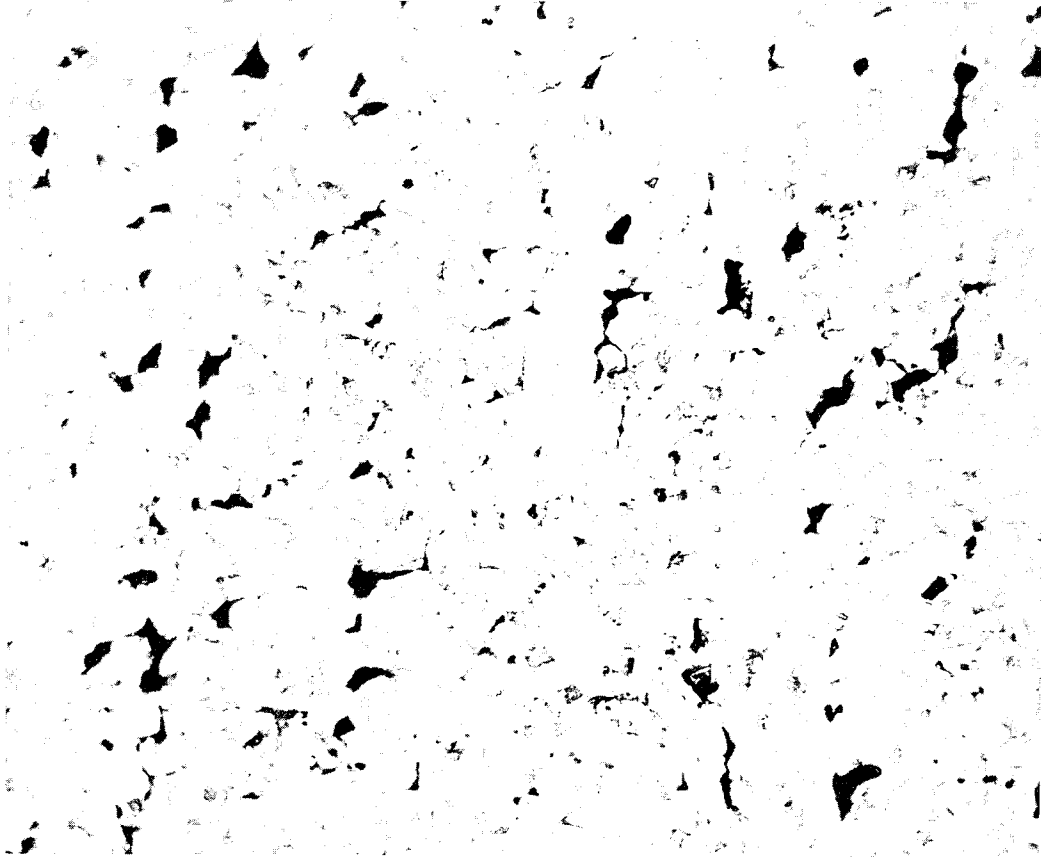


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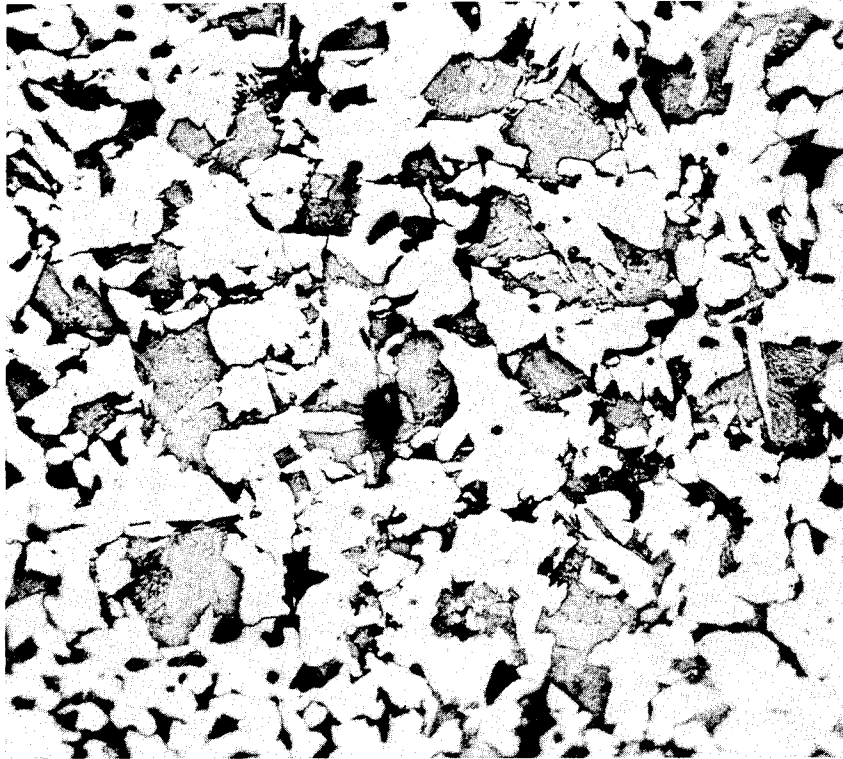


Fig. 2 - 1B Boiler - RW No.21 (Section through bulge that had cracked). Notice structure indicating that metal was rapidly cooled from temperature above 1335° F when the tube failed. Etchant: 1% Nital. 1000X.

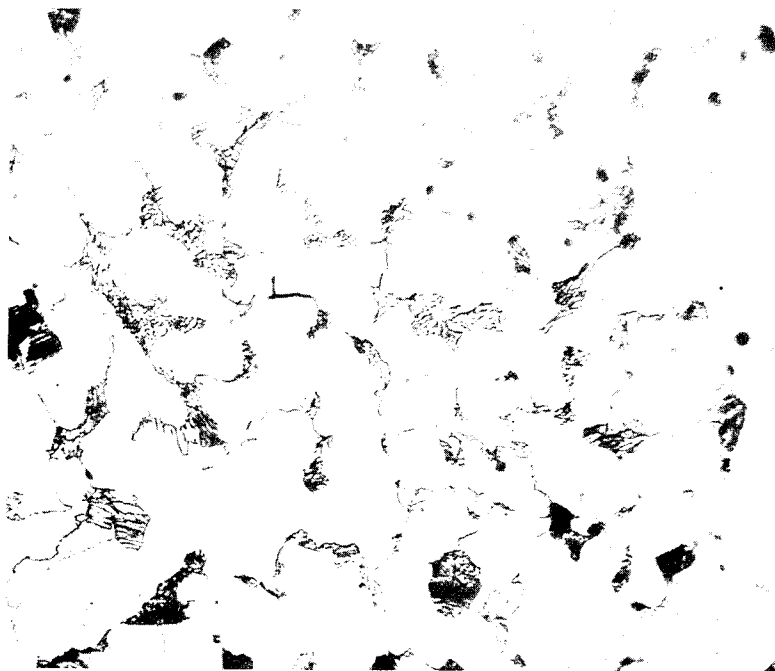


Fig. 3 - 1B Boiler - RW No.18 (Section through bulge that had not cracked). Note lamellar (new) pearlite which indicates that service temperature exceeded 1335⁰F. Etchant: 1% Nital plus 2% Picral. 1000X.

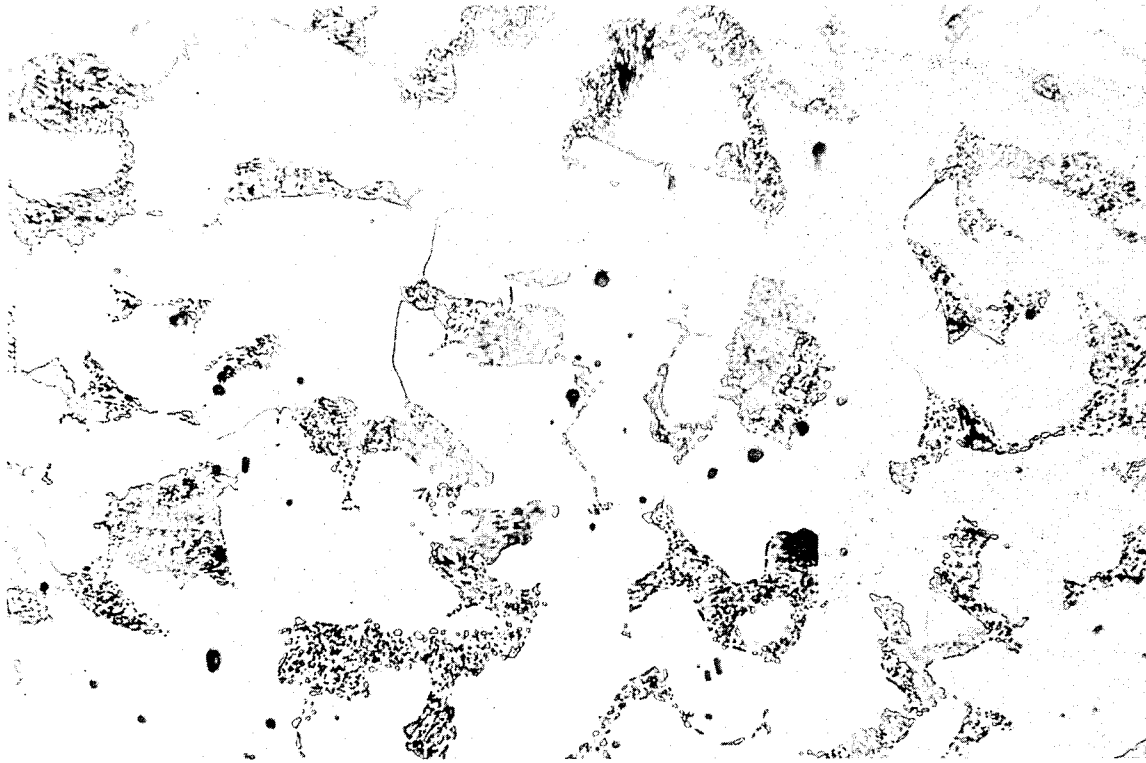


Fig. 4 - 1B Boiler - RW No. 18 (Section adjacent to bulge). Note coarse carbides; no evidence of partial austenitization is present. Etchant: 1% Nital plus 2% Picral. 1000X.

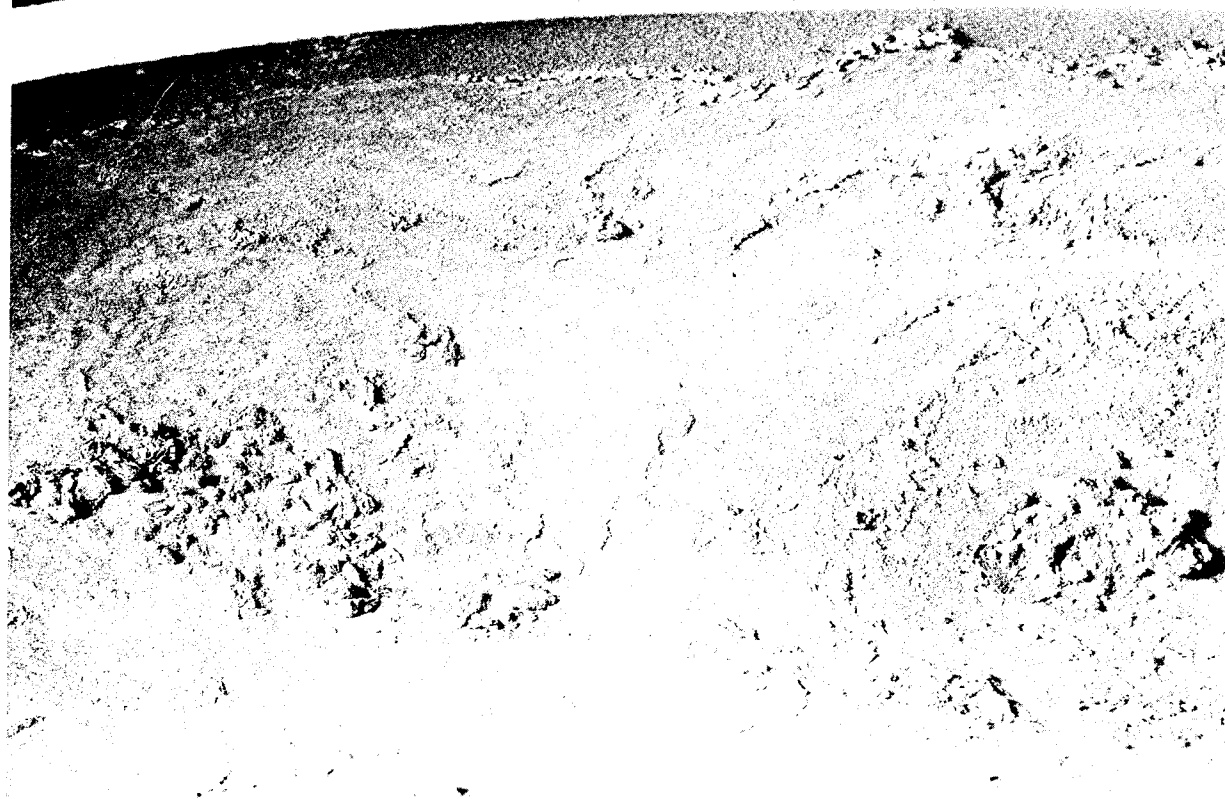


Fig. 5 - 1B Boiler - RW No. 30, Waterside
(Section containing two bulges). Note config-
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